SYNTHESIS OF Zn/Al_2O_3 NANOCOMPOSITE BY MECHANICAL ALLOYING ROUTE

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology
In

Metallurgical and Materials Engineering

Submitted by

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2011-2012

CERTIFICATE

This is to certify that the project entitled "Synthesis and Characterization of Zn/Al_2O_3 Nanocomposite by Mechanical Alloying Route " being submitted by Chandni and Gayatri Yadav, as an academic requirement in the Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela is a record of bonafide work carried out by the students under my guidance and supervision.

Prof. S.N. Alam

Dept. of Metallurgical and Materials Engineering

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Place: Rourkela

Date:

ACKNOWLEDGEMENT

We would like to express our sincere gratitude to Prof. S.N. Alam of the Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela, for providing us with this opportunity. We are thankful to him for his valuable suggestions and constructive criticisms from which we have derived benefits.

We would also like to thank our institution, NIT Rourkela, and all other faculty members for their support.

We would like to convey a special thanks to all our friends who have been extremely supportive and helpful.

Chandni (108MM039)

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ABSTRACT

Materials of nanostructure have novel properties which differ greatly from that of bulk materials. Due to high strength by weight ratio, they find useful applications in aerospace and automotive industries. Here, the purpose is to fabricate and characterize zinc based metal matrix nanocomposite by mechanical alloying route. ZnO and Al powder were taken in the stoichiometric ratio and milled in a planetary ball mill for 20h. During milling, displacement reaction takes place and forms Zn/Al_2O_3 nanocomposite. The ZnO reacts with Al through a self-sustaining combustion reaction process. As a result a Zn matrix composite reinforced by Al_2O_3 particles was produced. Further, the 20 h milled powder was also heat treated at 800^o C for 1h. The as-milled and heat treated powder was characterized by XRD, EDX, SEM and DSC.

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1. INTRODUCTION

There are several methods to develop metal matrix composites (MMCs). One of the favourable processes to fabricate particulate reinforced metal matrix composites (MMCs) is by addition of reinforcement particles to the metal matrix in the liquid state. In the liquid state process this can be achieved by addition of particulate reinforcements to the molten metal by stirring before casting. In this process uniform distribution is not possible if the particulate reinforcement is in nanometric dimension. Ultrasonic stirring, high-energy mechanical milling and internal oxidation are a few processes to get uniform distribution of the nano sized reinforcement particles in the molten metal. As such liquid state synthesis of metal matrix composite has been found to be difficult due to the difference in coefficients of thermal expansion between the reinforcement particles and the molten metal. The reinforcement particle which in many cases is a ceramic has poor wetability with the metal matrix. This is why the solid state route is favoured compared to the liquid state process. Mechanical milling is a solid state technique where it is possible to get a uniform distribution of the reinforcement particles in the metal matrix [1-6].

Here we used mechanical milling as a route to synthesize the Zn/Al_2O_3 metal matrix composite. Stoichiometric mixture of ZnO powder and Al powder

were milled in planetary ball mill. An exothermic displacement reaction takes place during milling. The chemical reaction is given below [7, 8].

$$3ZnO + 2Al \rightarrow Al_2O_3 + 3Zn$$

ΔG^{o}_{298}=-601704 J/mol

ΔH^{o}_{298}=-625509J/mol

Here the Zn metal matrix is reinforced by the Al_2O_3 particles. The solid metal oxide ZnO is reduced by Al resulting in the formation of Al_2O_3 and Zn. The milled powder is analyzed using SEM, EDX, XRD and DSC/TG. ZnO reacts with Al by a combustion reaction which is a self propagating high temperature process. The reaction between ZnO and Al as shown above is highly exothermic and it would be feasible to produce Al_2O_3 in Zn matrix giving rise to a Zn-Al_2O_3 nanocomposite [7-9].

2. **LITERATURE SURVEY**

2.1 Mechanochemical Synthesis

In metal matrix composites the addition of hard ceramic particles to soft metals provides a combination of the properties of both the metallic matrix and the ceramic reinforcement components. In our case also the Zn metal matrix is reinforced by Al_2O_3 ceramics particles. This enhances the physical and mechanical properties of the composite. Several methods have been developed to process metal matrix composites with ceramic reinforcements. Casting is one of the methods for preparation of such metal matrix composites. Apart from the difference in thermal expansion coefficients between the ceramic reinforcement particles and the metal matrix, the poor wettability between the two deters the favourability of the liquid state process. Apart from the casting route another way of producing metal matrix composite is by using powder metallurgy technique. In powder metallurgy technique, consolidation and sintering of the composite powder takes place to produce a composite part. Mechanical milling can be used for synthesis of the composite powder [10-12].

Mechanical milling is a solid state processing technique which takes place at room temperature. It involves repeated deformation, welding and fracturing of the powder particles. In mechanical milling mechanically induced solid state chemical reaction occurs in the powder mixture charged in vials.

Here energy is provided by the collision in the grinding media. Mechanical milling leads to a very uniform distribution of the reinforcement particles in the matrix. Nanocomposites can be developed using mechanical milling. Considerable research has been done on development of nanocomposites using mechanical milling.

Mechanical milling is mainly of three types. In mechanical milling process there is no change in the chemical composition of the charged powder during milling. In mechanical alloying alloys can be synthesized by milling of the charged material. In mechanochemical synthesis process the chemical composition of the charged powder changes as a result of energy from impacts during milling. This process is also called as reactive milling. Here in our case, the milling of ZnO and Al, leads to the formation of Al_2O_3 and Zn. This is also an example of reactive milling or mechanochemical synthesis. This is an example of self propagating high temperature synthesis (SHS) process [8-10].

The two types of chemical reactions that take place in mechanochemical reactions are non-displacement and displacement chemical reactions. Nondisplacement reactions are those chemical reactions where a combination of reactant elements takes place to produce the final product phase. However, in displacement reaction an interchange of elements among reactants occur to create the new product phases.

$$MO + R = RO + M$$

Our case also is also an illustration of a displacement reaction. A more reactive metal (R) is reduces the metal oxide (MO) to the pure metal M. The products of displacement reactions in our case consists of two phases, the metal and metal oxide, though chlorides or sulphides of metals could also be formed. The products of mechanochemical reaction maybe used to develop a composite. The oxide phases may serve as reinforcement in MMC. Mechanochemical synthesis succeeds over other processes. Mechanochemical synthesis is a solid state process which takes place at room temperature. This is its foremost advantages over the other techniques. Consequently it gives the prospect of producing a nanocomposite [10, 13-16].

2.2 Reaction Kinetics of Mechanochemical Synthesis

Thermodynamically, mechanochemical reactions are very viable at room temperature due to enormous negative free energy change. The mechanism of mechanochemical process consists of recurring deformation, fracture and welding of the powder particles during collisions of the grinding media. During the course of milling large particles get broken down to smaller particles. Thus generating enormous surface area act as reaction sites. This lowers down the

activation energy. Diffusion takes place between adjacent particles. This diffusion is also assisted due to large number of defects generated by milling. High concentration of defects in the lattice generated by milling enable diffusion to take place.

Kinetically a mechanochemical reaction can be classified as gradual or sudden reaction. Various factors determine the type of reaction kinetics like reactants, enthalpy change and milling condition.

If the enthalpy change accompanied by the reaction is small, the heat generated produced will not affect the reaction kinetics appreciably. Thus our reaction progresses in a gradual mode. Due to refining of reactants and diminishing activation energy, the reaction rate in the beginning of reaction increases tremendously. It attains the maximum rate after an intermediate time of milling and then decreases as the reaction comes to an end.

Collision of milling media produces heat. If this heat produced is enormously high (enthalpy change is high), the rate of reaction is very fast. For reactions accompanied by the high enthalpy change, the temperature of the vials increases rapidly due to combustion of reactants. Moreover, as these reactions are exothermic in nature large amount of heat energy is generated. This makes

them self propagating reactions. With the completion of reactions, temperature drops down slowly [10-16].

2.3 Milling Equipments

Ball milling equipments can be classified as “low energy” and “high energy” depending upon the mechanical energy provided to the precursor powder during milling. The horizontal mill is a low energy mill whereas attrition, planetary and vibratory mills are high energy ball milling equipments. High energy ball milling is preferred if a change in chemical composition of reactants is desired. Here in our case, we have used a planetary ball mill. This is a high energy ball milling equipment where vials and disc rotate in opposite direction. The sense of direction for rotation of vials on its axis is opposite to the direction of its revolution around the disc’s axis [1-5, 10, 17].

3. EXPERIMENTAL INSTRUMENTS

3.1 Planetary Ball Mill

In a planetary ball mill the grinding of the charged powder takes place by the impact of the balls on the charged powder in the revolving vials. Here for our milling purpose we have used a Fritsch Pulverisette planetary ball mill. The vials and balls that have been used are made of chrome steel. The milling medium was toluene. The ratio of ball weight to charge weight was maintained at 10:1 and milling was done at 300RPM for a maximum period of 20 h [1-5, 10, 17].

3.2 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX):

A scanning electron microscope (SEM) is a type of electron microscope. Images of a sample are formed by scanning it with a high-energy electron beam. The electron beam interacts with the atoms of the sample. Image of the sample can be formed from the signals that are generated by the interaction of the electron beam with the sample. The SEM image gives us information regarding the sample's surface topography, Composition of the sample can also be found out.

Very high-resolution images of a sample surface can be produced using SEM. SEM images have a large depth of field [18-22].

SEMs also have the ability to analyse particular points as can be seen during EDS operations which help in determining the chemical composition of the sample concerned. EDS analysis was performed on a Jeol T-300 scanning electron microscope using an Oxford INCAPentaFET-X3 energy-dispersive X-ray spectroscopy system with a high-angle ultrathin window 30 mm2 Si(Li) X-ray detector that was liquid-nitrogen cooled. An accelerating voltage of 25 kV was used with a 1 nm probe with ~1 nA of current on the specimen [23-24].

The internal arrangement of SEM is shown below in Fig. 1. The various components of a SEM are as follows:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:

a) Power Supply

b) Vacuum System

c) Cooling system

d) Vibration-free floor

e) Room free of ambient magnetic and electric fields.

Fig. 1: JEOL JSM-6480LV Scanning Electron Microscope.

The JEOL JSM-6480LV SEM shown in Fig. 4 was used for microscopoical analysis of the samples.

3.3 Differential Scanning Calorimetry:

Differential scanning calorimetry (DSC) is a thermo analytical technique wherein the difference in the amount of heat needed to raise the temperature of a sample and a reference material is measured as a function of temperature.

Both the sample and reference are maintained at nearly the same temperature throughout the experiment. The temperature of the sample holder of a DSC program for analysis increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned [25].

3.4 X-ray Diffraction Techniques:

X-ray diffraction (XRD) is a non-destructive technique which provides information regarding the crystal structure of a substance. X-ray diffraction gives us information like lattice parameter, chemical composition and crystal structure of the material. XRD is based on the principle of constructive interference of x-rays. The x-rays which are generated are filtered, collimated and then directed towards the sample. The interaction of the x-rays with the sample produces x-ray peaks at particular angles. Bragg's law relates the wavelength of the x-ray with the interplanar spacing and the diffraction angle. Bragg's law states that,

$$\lambda=2d\mathrm{Sin}(\theta)$$

Where,

λ =wavelength

d=interplanar spacing

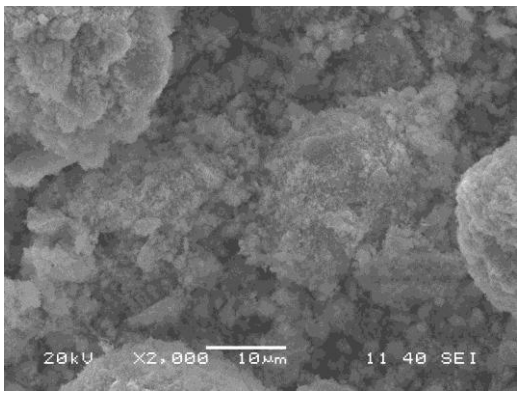
θ=diffraction angle

X-ray diffraction (XRD) analysis of the samples were also done in order to track the formation of new phases with oxidizing temperature [26-27]. A Philips Pananalytical X'Pert X-ray diffractometer using CuKα radiation (λ = 0.15406 nm) was used.

4. RESULTS AND DISCUSSION

The objective of this study is to synthesize Al_2O_3 in-situ in Zn matrix. ZnO and Al powder are taken in the proper stoichiometric ratio and milled for 20 h in a Fritsch pulverisette planetary ball mill. The SEM images in Figs.2(a-c)-5(a-c) show the morphology of the powder milled for various periods of time. It can be clearly seen that with increased milling time the particles have sharper edges and flake like structures can be seen in the 15 and 20 h milled powders. The EDX along with the SEM images show the presence of all three elements O, Al and Zn in the milled powder. The milled product shows the gradual reduction in particle size.

(a)



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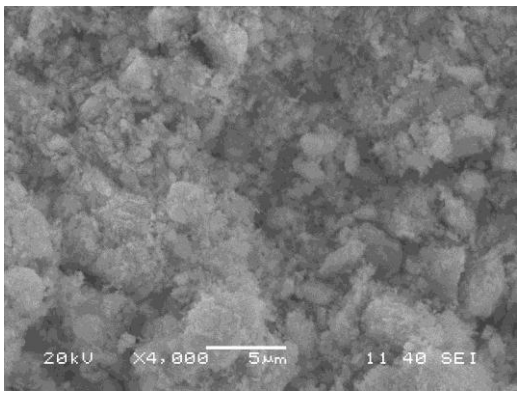


(c)

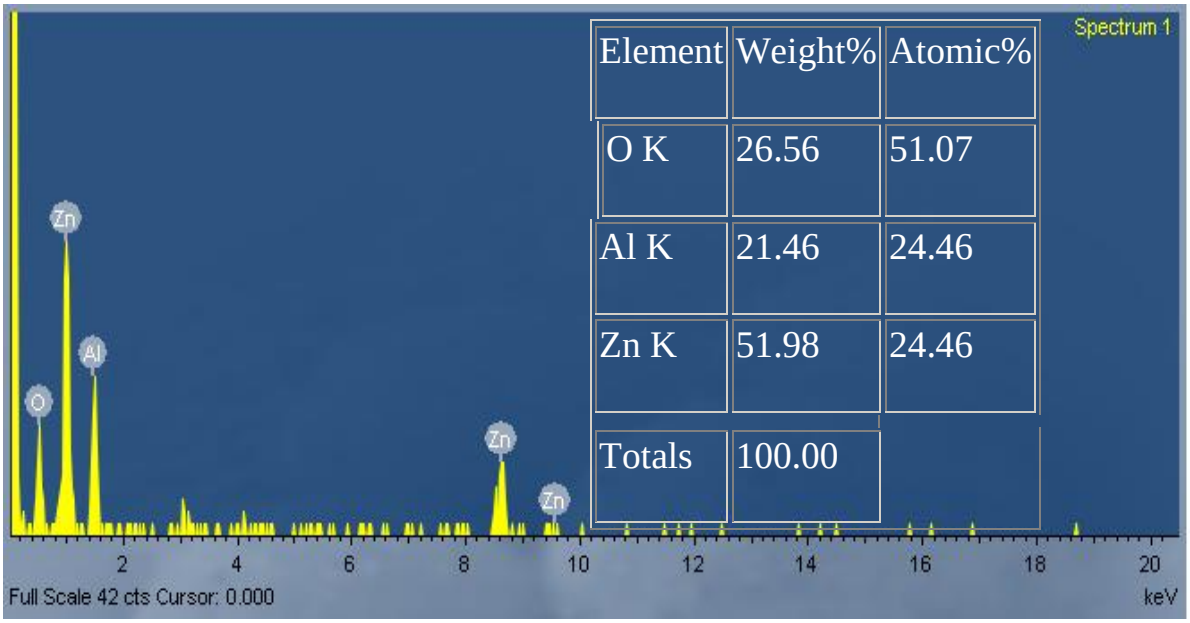
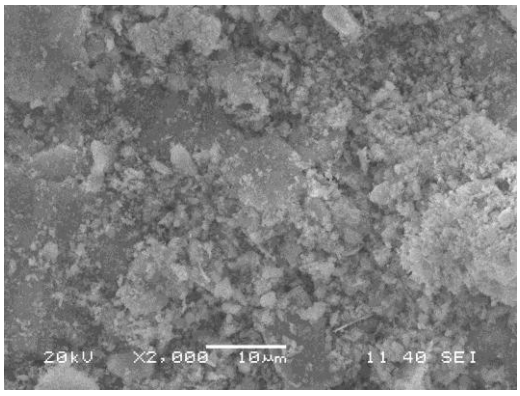


Fig.2(a-b) SEM images of 6 h milled powder and (c) EDX from the milled powder.

(a)



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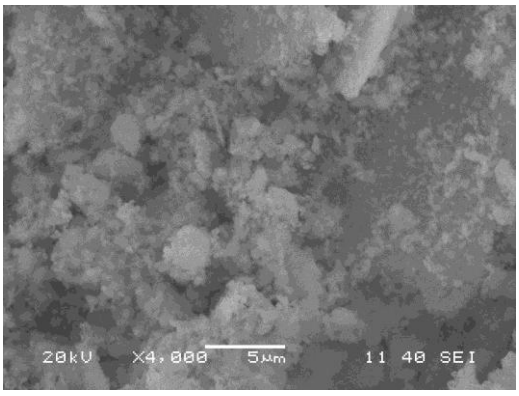


(c)

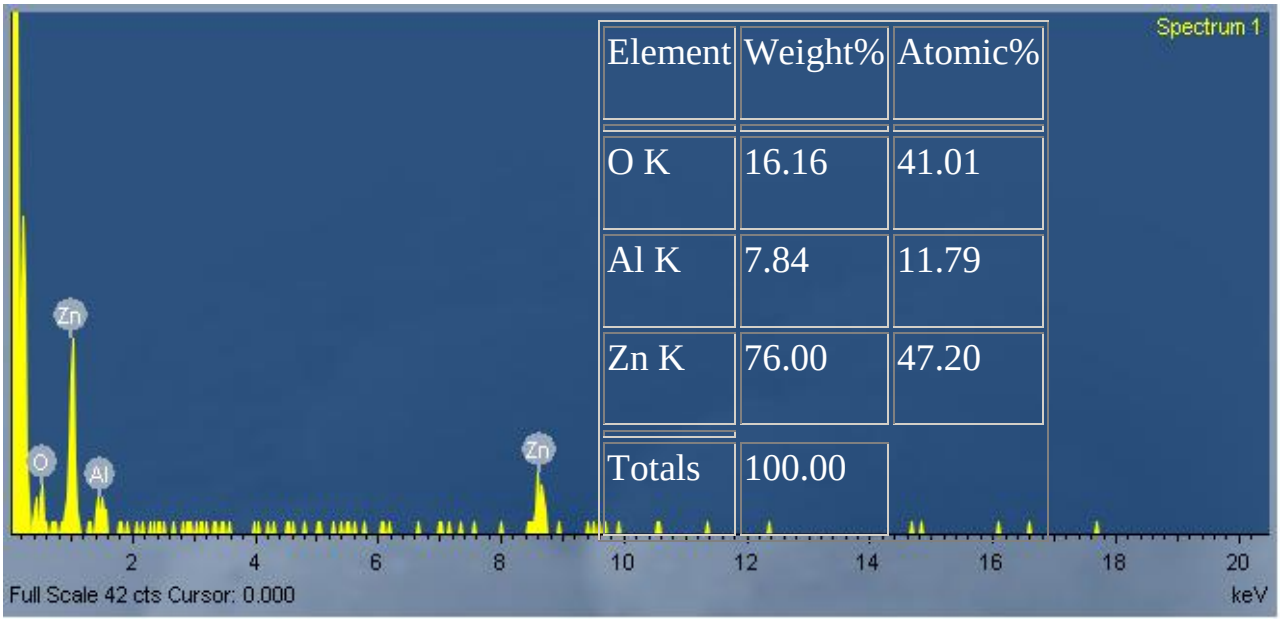
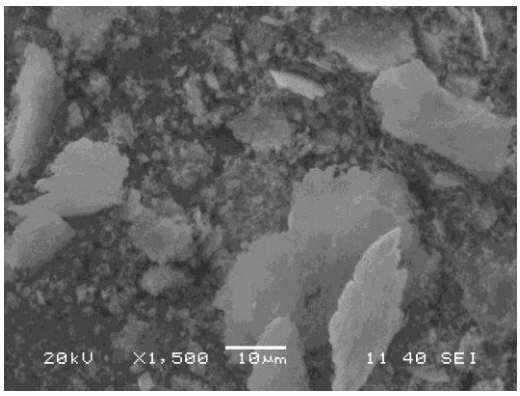


Fig.3(a-b) SEM images of 10 h milled powder and (c) EDX from the milled powder.

(a)



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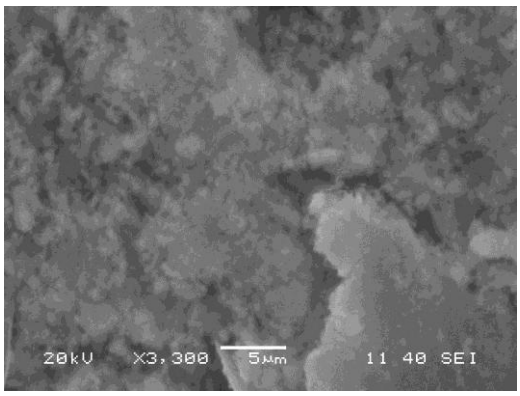
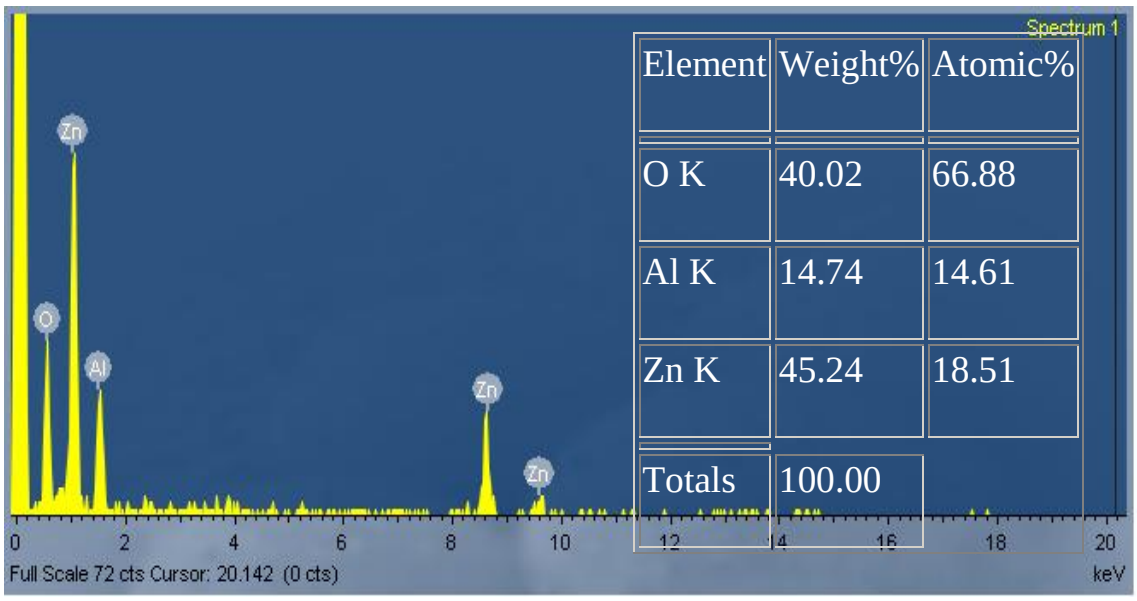


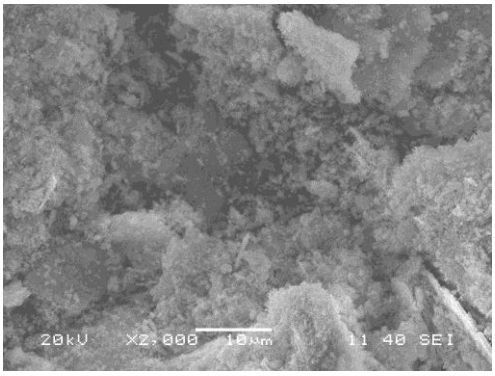
(c)



Element	Weight%	Atomic%
O K	40.02	66.88
Al K	14.74	14.61
Zn K	45.24	18.51
Totals	100.00	

Fig.4(a-b) SEM images of 15 h milled powder (c) EDX from the milled powder.

(a)



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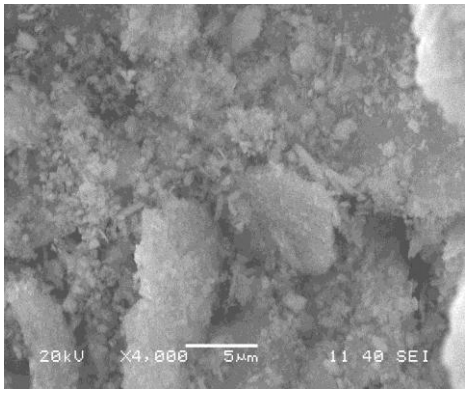


(c)

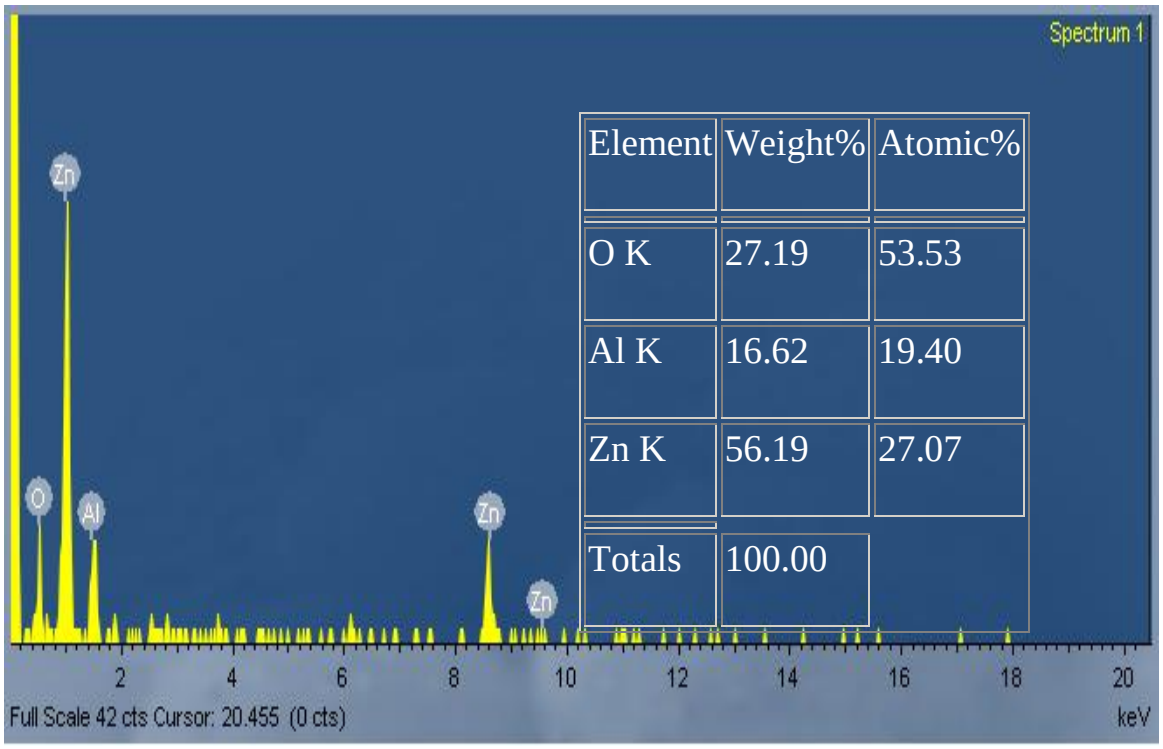


Fig.5(a-b) SEM images of 20 h milled powder and (c) EDX from the milled powder.

The XRD plot in Fig.6 suggests that it was not possible to convert the entire Al into Al_2O_3 after 20 h of milling in chrome steel vials and balls and there is possibly some amount of Al remaining after 20 h of milling. Also there is very little amount of Zn detectable after 20 h of milling. All this suggests that after 20 h of milling the entire amount of ZnO has not been reduced by Al. This is why the 20 h milled powder was heat treated at 800^{o}C for 1 h in inert atmosphere of Ar to see if complete transformation of all the Al to Al_2O_3 is possible. Although it was found that significant amount of the Al after heat

treatment of the 20 h milled powder transformed into Al_2O_3 there was still certain amount of Al that remained untransformed. More peaks of Zn are now visible in the XRD plot suggesting that a significant amount of ZnO has transformed to Zn due to the reduction by Al, after the 20 h milled powder was heat treated at 800^{o}C for 1 h.

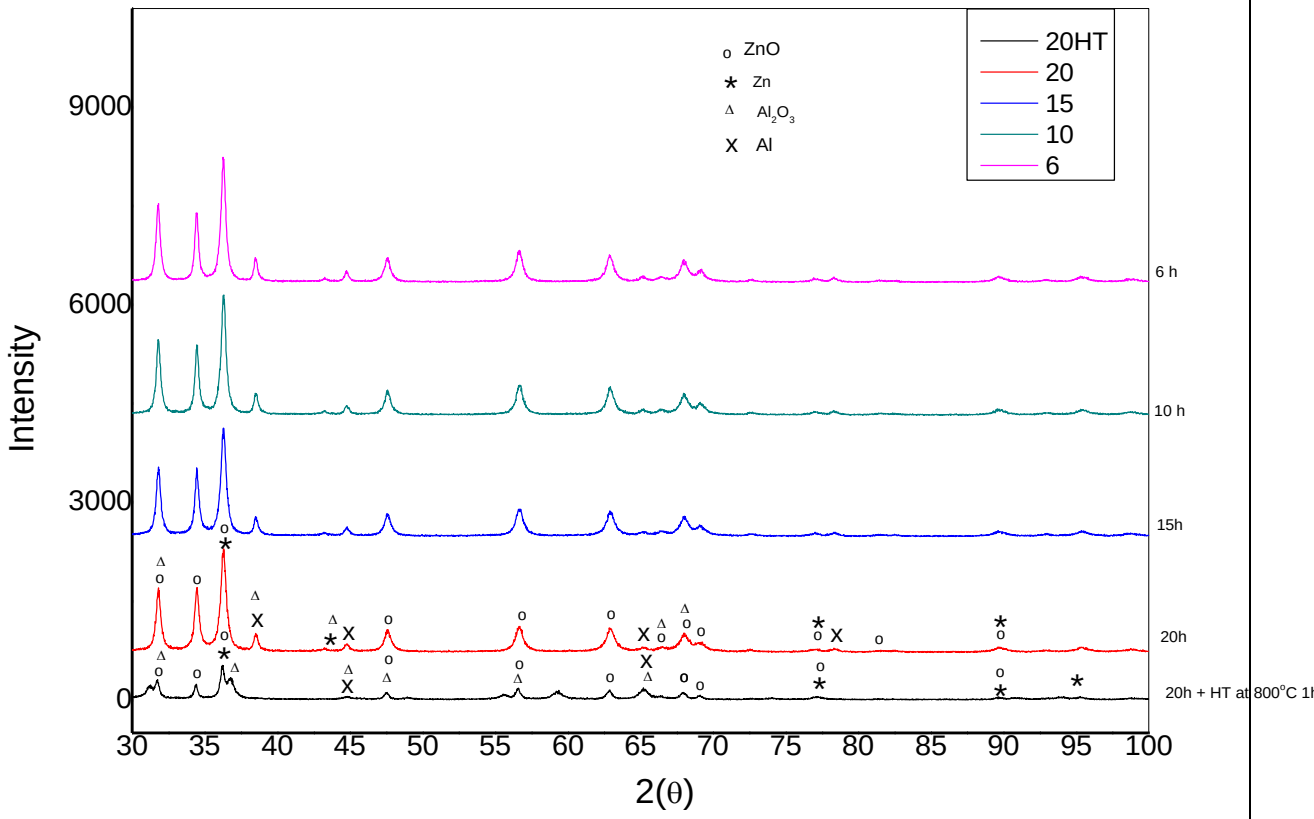


Fig.6 XRD plots of ZnO and Al powder milled for 20 h and 20 h milled powder heat treated at 800^{o}C for 1 h.

The DSC/TG of 6 h milled powder is shown in Fig.7. It suggests that ordered crystalline Al_2O_3 is formed by an exothermic reaction at a temperature of 588.5^{o}C. This exothermic peak is due to the heat released when amorphous

Al_2O_3 transforms to crystalline Al_2O_3 (Tavoosi, Karimzadeh). The peak is very sharp. DSC of the 20 h milled powder was also done (Fig.8). The DSC plot of the 20 h milled powder was wider. The TG plot shows a gain in weight of 1.39%. in the case of 6 h milled powder and 2.71% in the case of 20 h milled powder. This is possibly due to the oxidation of the powder.

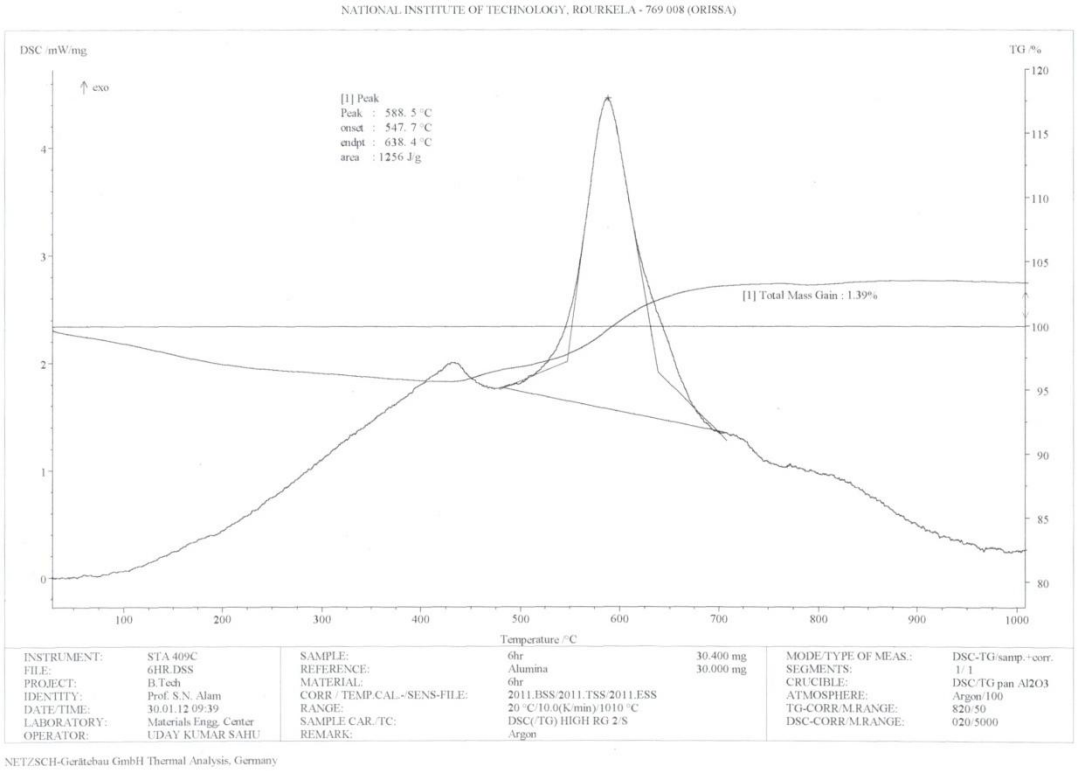


Fig.7 DSC and TG of 6 h milled sample.

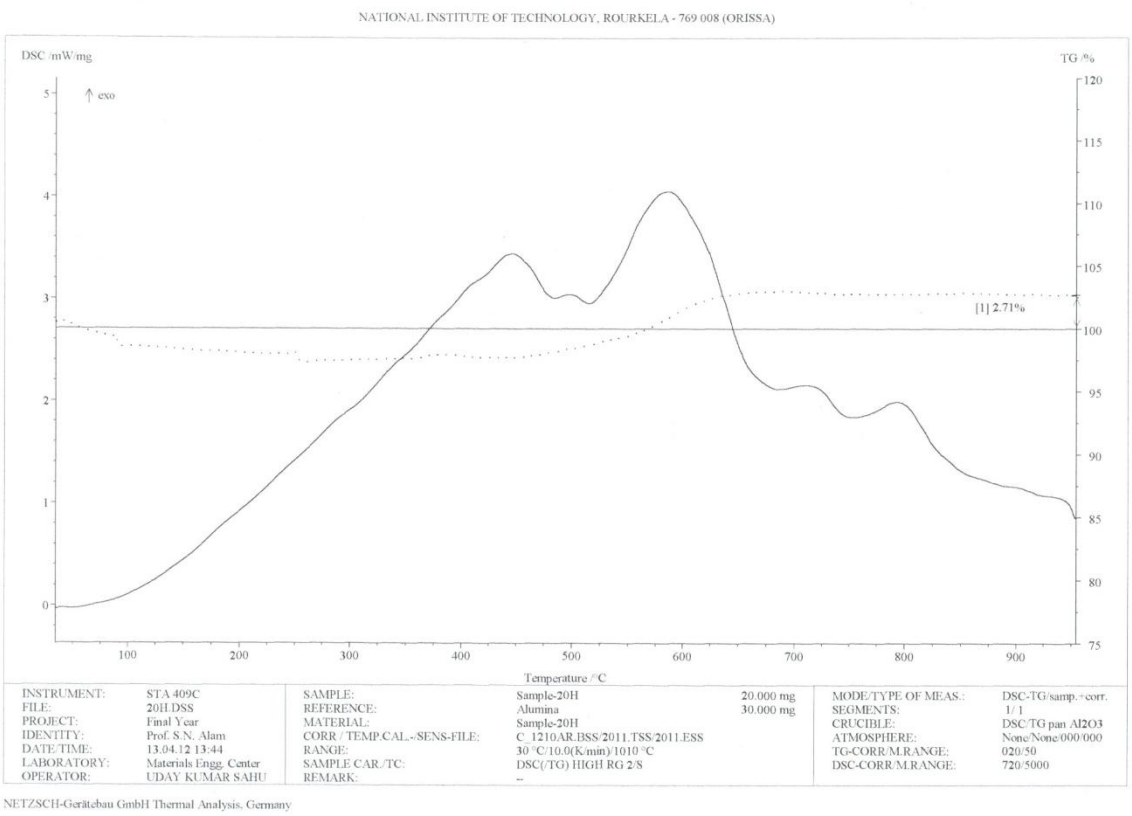
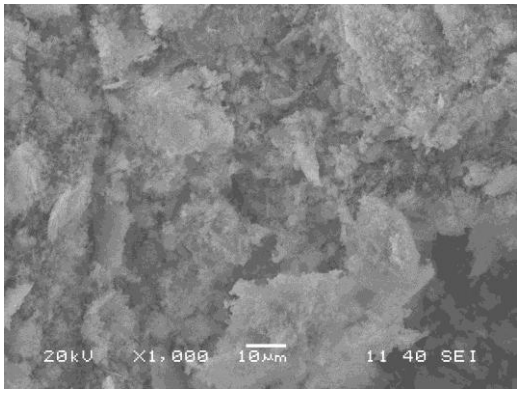


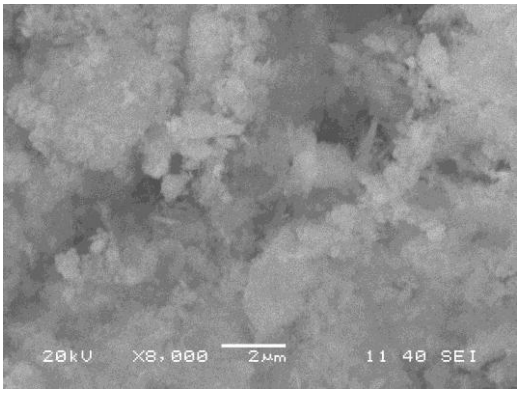
Fig.8 DSC and TG of 20 h milled sample.

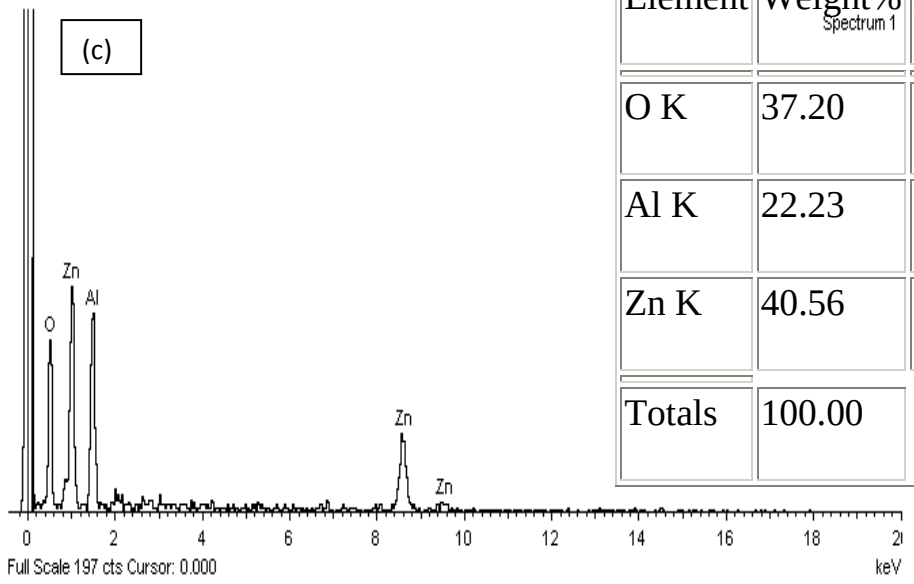
The SEM images in Fig.9(a-b) show the morphology of the 20 h milled powder heat treated at 800^{o}C for 1 h. Fig. 8(c) is the EDX from the sample.

(a)



(b)





Element	Weight% Spectrum 1	Atomic%
O K	37.20	61.68
Al K	22.23	21.86
Zn K	40.56	16.46
Totals	100.00	

Fig. 9(a-b) SEM images if 20 h milled powder followed by heat treatment at 800^{o}C for 1 h (c) EDX from the sample.

5.0 CONCLUSION

1. It was possible to transform a significant amount of Al to Al_2O_3 after heat treatment of the 20 h milled powder at 800^oC for 1 h. Zn could also be traced in the heat treated powder.
2. Although a significant amount of Al was transformed to Al_2O_3 after heat treatment of the 20 h milled powder there was still certain amount of Al that was left. Certain amount of ZnO was also not reduced. The absence of high intensity Zn peaks suggest that not all the ZnO has been reduced by Al into Zn and Al_2O_3.
3. The DSC results suggest that highly crystalline Al_2O_3 could be formed.

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